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The Meerwein–Ponndorf–Verley–Oppenauer reaction between 2-hexanol and cyclohexanone on magnesium phosphates

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Various magnesium phosphates were tested as catalysts for the vapour-phase Meerwein–Ponndorf–Verley–Oppenauer (MPVO) reaction between 2-hexanol and cyclohexanone. Some of the solids studied are as selective as MgO in this reaction. Others are also active in the dehydration of the alcohols. The activity and selectivity of the catalysts are related to their structure and surface chemical properties.

Keywords: magnesium phosphates, magnesium oxide, Meerwein–Ponndorf–Verley–Oppenauer reaction, dehydration, dehydrogenation, 2-hexanol, cyclohexanone

1. Introduction

A number of magnesium phosphate catalysts are used in various organic processes. One such process is the oxidative transformation of methane [1], where increasing acidity in the catalyst has been found to shift the reaction from dimerization to selective oxidation. A commercially available magnesium phosphate was used for the oxidative dehydrogenation of ethane and the oxidative coupling of methane [2,3]. The presence of chlorinated species on the catalyst surface was found to improve its catalytic properties. Similar solids have been used in the dehydration–dehydrogenation of alcohols, where activity and selectivity depend on the structure and composition of the catalyst employed [4].

The transfer of hydrogen between an alcohol and an aldehyde or ketone is known as the Meerwein–Ponndorf–Verley (MPV) reaction. It takes place in a homogeneous phase containing a metal alkoxide of which aluminium isopropylate provides the best results. A number of heterogeneous catalysts such as oxides [5–8] and zeolites [9–12] have also been used for this purpose. The reverse reaction, i.e., the oxidation of alcohols via the same mechanism, is known as the “Oppenauer oxidation”. One typical example is the use of excess propionaldehyde as hydrogen acceptor in the dehydrogenation of long-chain aliphatic alcohols on MgO to obtain the corresponding aldehydes (C_9–C_{12}), which are of interest to the perfumery industry [13].

The mechanism for the MPVO reaction in both homogeneous and heterogeneous media involves an intermediate complex, where a metal ion acting as a Lewis acid binds to the alkoxide and carbonyl compound, and a hydride ion is subsequently transferred from the former to the latter [14].

This reaction has been used as a prototype of base-catalysed processes [15] and as a test reaction in studies on the basicity of heterogeneous catalysts [16]. The reaction also develops in the presence of Lewis acid catalysts but is more efficient with basic ones, as they exhibit stable activity and give no side reactions.

This paper reports the results obtained in the MPVO reaction between 2-hexanol (2-HOL) and cyclohexanone (CHONE) on several magnesium phosphates of differential structure and properties. The results are compared with those provided by MgO.

2. Experimental

2.1. Materials

We used three commercially available solids of formula $Mg_3(PO_4)\cdot xH_2O$ (Aldrich reference 34,470-2), $MgHPO_4\cdot 3H_2O$ (Aldrich reference 34,075-8) and $Mg(OH)_2$ (Probus reference 3225), which, once calcined, were designated MgP_C, $MgPP_C$ and MgO_C, respectively.

The other solids studied were obtained by gelling of reactant solutions in combination with various treatments. Thus, solid $MgP_{(OH,H)}$ was prepared by dropwise addition of 51.6 ml of an H_3PO_4 solution in 100 ml of water over a suspension containing 66.6 g of $Mg(OH)_2$ in 400 ml of distilled water under continuous stirring. Following stirring for a further 3 h, the mixture was allowed to stand for 24 h and filtered. The solid was then washed with 1 l of water and air-dried. Solid $MgP_{(Cl,H)}$ was synthesized by adding a 3 N NaOH solution over one containing 80 g of $MgCl_2\cdot 6H_2O$ and 17.8 ml of H_3PO_4 in 200 ml of water, placed in an ice bath, until pH 9 was reached. After 24 h of standing, the solid was filtered and air-dried. Solid $MgP_{(Cl,H,w)}$ was prepared similarly to the previous one except for additional washing with distilled water (20 ml/g-solid) for 30 min, followed by standing for 24 h and air-drying. Solid $MgP_{(Cl,H,C,w)}$ was prepared by using the previous procedure but Na_2CO_3 as the precipitant. Thus, a 1.6 N

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solution of Na_2CO_3 was added over one containing 62.6 g of $MgCl_2{\cdot}6H_2O$ and 13.9 ml of H_3PO_4 in 500 ml of water up to pH 9. The solid thus obtained was filtered, washed with 500 ml of distilled water and air-dried. Finally, solid NaMgP was synthesized by precipitating a solution containing $MgCl_2$ and Na_2HPO_4 with NaOH, followed by digestion with Na_2CO_3, as described elsewhere [4].

All solids were calcined stepwise up to 773 K and sifted through 200–250 mesh. The products thus obtained were characterized by XRD, thermal analysis, SEM and EDAX and analysis, and DRIFT spectroscopy. Their specific surface areas were determined by using the BET method on a Micromeritics ASAP 2000 analyser.

Acid and basic sites in the solids were quantified from the retention isotherms for cyclohexylamine and phenol, respectively, dissolved in cyclohexane. The amount of titrant retained by each solid was measured spectrophotometrically ($\lambda_{\max} = 226$ and 271.6 nm for cyclohexylamine and phenol, respectively). By using the Langmuir equation, the amount of titrant adsorbed in monolayer form, X_m, was obtained as a measure of the concentration of acid and basic sites [17].

2.2. Catalytic reactions

Reactions were carried out in a glass tubular reactor of 6 mm ID that was fed at the top with a 2-hexanol/cyclohexanone equimolar mixture by means of a SAGE propulsion pump the flow-rate of which was controlled via a nitrogen flowmeter. Evolved gases from the reactor were passed through a condenser and onto a collector that allowed fluids to be withdrawn at different times.

No diffusion control mechanism was detected [18], nor was any of the reactor elements found to contribute to the catalytic effect under the reactor's operating conditions used in preliminary blank runs (viz. feed rate 1–10 $\mathrm{ml\,h^{-1}}$, $T =$ 575–773 K, N_2 flow-rate 40 $\mathrm{ml\,min^{-1}}$, amount of catalyst 0.1–0.5 g).

Collected samples were analysed by gas chromatography, using an SPB-5 60 m$\times$0.25 mm ID phenylsilicone capillary column and raising the temperature from 308 to 433 K at 15 $\mathrm{K\,min^{-1}}$. The reaction products detected included 2-hexanone (2-HONE), cyclohexanol (CHOL), cyclohexene (CHE) and various hexenes (HENES) – the last resulted from isomerization of the initially produced 2-hexene (Z + E) to other hexene isomers.

3. Results and discussion

3.1. Catalyst characterization

Table 1 lists the major phases found in the catalysts studied and summarizes their surface chemical properties. As can be seen, the catalysts consist of various crystal phases. $Mg_3(PO_4)_2$ solids with a farringtonite structure become amorphous on calcination at 773 K. Such a crystal phase can only be detected above 923 K. This structure is shared by solids MgP_C, $MgP_{(OH,H)}$, $MgP_{(Cl,H)}$, $MgP_{(Cl,H,w)}$ and $MgP_{(Cl,H,C,w)}$. Unlike the others, solid $MgP_{(Cl,H)}$ contains 4.4% of sodium (possibly as sodium–magnesium mixed phosphates). Catalyst $MgPP_C$ consists of α-$Mg_2P_2O_7$, which results from the calcination of $MgHPO_4{\cdot}3H_2O$ at 773 K. Finally, catalyst MgO_C possesses a periclase MgO structure that results from calcination of $Mg(OH)_2$ above 660 K.

Most of the solids studied possess a very low specific surface area; the area exceeds 30 $\mathrm{m^2\,g^{-1}}$ in none of the magnesium orthophosphates. Only the magnesium oxide MgO_C, obtained by calcining commercially available $Mg(OH)_2$ at 773 K, has a fairly high surface area.

All the magnesium orthophosphates studied contain more acid sites than basic sites on their surface. Only in the periclase MgO solid is the population of basic sites larger than that of acid sites.

3.2. Catalytic activity

Table 2 summarizes the catalytic activity results for the solids. The product distribution found can be explained on the basis of scheme 1. The MPV reaction between 2-hexanol (2-HOL) and cyclohexanone (CHONE) to give 2-hexanone (2-HONE) and cyclohexanol (CHOL) can be accompanied by various side reactions. Thus, 2-hexanol

Table 1
Structure, surface chemical properties and major phases present in the solids studied.[a]

Catalyst	Phase [structure]	S_{BET} ($\mathrm{m^2\,g^{-1}}$)	Acidity[b] ($\mu\mathrm{mol\,g^{-1}}$)	Basicity[c] ($\mu\mathrm{mol\,g^{-1}}$)
MgP_C	Amorphous [$Mg_3(PO_4)_2$]	7	24	6
$MgP_{(OH,H)}$	Amorphous [$Mg_3(PO_4)_2$]	6	27	9
$MgP_{(Cl,H)}$	Amorphous [$Mg_3(PO_4)_2$, $NaMg_4(PO_4)_3$ (?)]	9	23	11
$MgP_{(Cl,H,w)}$	Amorphous [$Mg_3(PO_4)_2$]	31	83	44
NaMgP	$NaMgPO_4$	8	12	5
$MgPP_C$	α-$Mg_2P_2O_7$	11	51	9
$MgP_{(Cl,H,C,w)}$	Amorphous [$Mg_3(PO_4)_2$]	30	134	40
MgO_C	Periclase MgO	241	123	254

[a] All solids were calcined at 773 K.

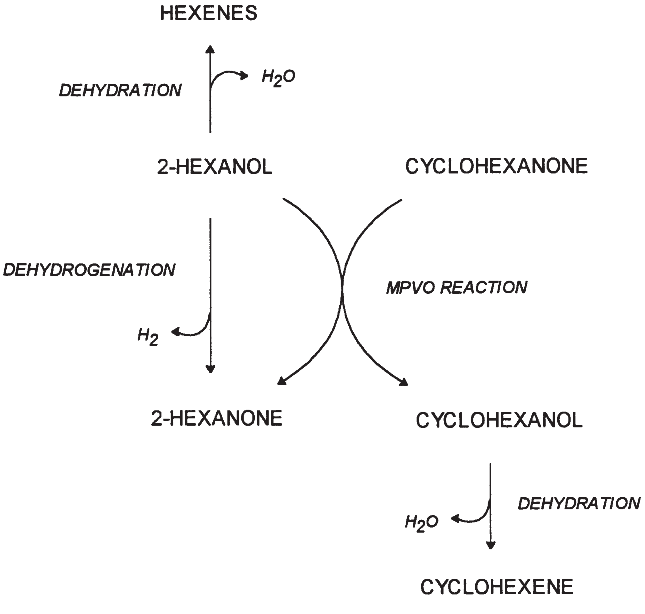
[b] Versus cyclohexylamine.

[c] Versus phenol.

Table 2
Activity and selectivity in the hydrogen transfer.[a]

Catalyst	T_{reac} (K)	For donor $X_{2\text{-HOL}}$	For donor $S_{2\text{-HONE}}$	For donor S_{HENES}	For acceptor X_{CHONE}	For acceptor S_{CHOL}	For acceptor S_{CHE}
MgP_C	623	4.0	74.0	26.0	3.0	88.8	11.2
MgP_C	673	14.0	68.0	32.0	8.4	67.6	32.2
MgP_C	773	74.9	31.0	69.0	20.5	22.9	77.1
$MgP_{(Cl,H)}$	623	5.8	100.0	–	5.8	100.0	–
$MgP_{(Cl,H)}$	673	13.8	98.6	1.4	13.6	97.2	2.8
$MgP_{(Cl,H)}$	723	54.9	98.6	1.5	54.3	95.8	2.5
$MgP_{(Cl,H,w)}$	673	68.8	93.8	6.3	64.6	75.5	24.5
NaMgP	673	4.5	100.0	–	4.5	100.0	–
NaMgP	773	37.0	100.0	–	26.0	100.0	–
$MgP_{(Cl,H,C,w)}$	673	100.0	7.0	93.0	1.9	1.6	98.4
$MgPP_C$	673	100.0	0.7	99.3	0.4	6.7	93.3
$MgP_{(OH,H)}$	673	7.4	29.7	70.3	2.0	74.7	25.2
MgO_C	673	69.9	100.0	–	69.8	100.0	–

[a] Reaction conditions: W/F (2-HOL feed $mol^{-1}\,h\,g_{cat}$) $= 2.82$; N_2 flow rate 40 ml min^{-1}; amount of catalyst 0.175 g; feed rate 3.88 ml h^{-1}, $t_{reac} = 120$ min. $X_{2\text{-HOL}}$, total conversion for 2-HOL; X_{CHONE}, total conversion for CHONE; S_i, selectivity towards compound i.



Scheme 1. Distribution of reaction products.

can be directly dehydrogenated to 2-hexanone; also, the donor alcohol (2-hexanol), or that resulting from the MPV reaction (cyclohexanol), can be dehydrated to hexenes (HENES) and/or cyclohexene (CHENE), respectively.

Table 2 gives the total conversion for the donor and acceptor, as well as the selectivity achieved with each solid, at different temperatures. All values shown were obtained at $t = 120$ min, beyond which conversion remained constant.

The solids studied can be grouped according to catalytic behaviour (selectivity) in the MPVO reaction. Thus, $MgP_{(Cl,H)}$, NaMgP and MgO_C are highly selective towards the hydrogen transfer in the MPVO reaction. Solid $MgP_{(Cl,H,w)}$ is also quite selective for this process. On the other hand, $MgP_{(Cl,H,C,w)}$ and, especially, $MgPP_C$, are scarcely selective towards this process and tend to promote the dehydration of 2-hexanol instead.

The joint consideration of the catalytic activity data of table 2 and the surface chemical properties of table 1 allows one to draw several interesting conclusions. Broadly speaking, the solids that are scarcely active in the MPV reaction (viz. $MgP_{(Cl,H,C,w)}$ and $MgPP_C$) possess a high density of acid sites (4.5 and 4.6 $\mu mol\,m^{-2}$, respectively) and a high acid-to-basic site ratio (3.3 and 5.7, respectively). These catalysts are highly active in the dehydration of alcohols and yield hexenes quantitatively. $MgP_{(Cl,H,C,w)}$ gives a small amount (ca. 2%) of cyclohexanone. Among the phosphates, solids $MgP_{(Cl,H)}$ and NaMgP exhibit the lowest surface densities of acid sites (2.5 and 1.5 $\mu mol\,m^{-2}$), and solid $MgP_{(Cl,H,w)}$ a density of 2.7 $\mu mol\,m^{-2}$.

Catalyst MgO_C is essentially basic, even though it contains weak Lewis acid sites [19]. This solid is highly active and selective in the MPVO reaction. Niyama and Echigoya [7] reported a mechanism involving hydrogen-bonded species where the alcohol was adsorbed at O^{2-} basic sites and the ketone at OH Brønsted sites. This mechanism requires the two types of sites to be close enough to each other and slightly acidic surface hydroxyl groups to be present. Ivanov et al. [16] suggest that these active OH groups result from the dissociative adsorption of the alcohol, Mg^{2+} ions acting as Lewis acid sites and O^{2-} ions as basic ones. Consistent with the results of these and other authors [20], our data suggest that the presence of basic sites is indispensable for the reaction to take place.

NaMgP and $MgP_{(Cl,H)}$ are the most selective phosphates in the MPVO reaction. The former possesses an $NaMgPO_4$ structure and, as shown elsewhere [4,21], is essentially basic. The basicity of these solids can be ascribed to the presence of M–O–P groups with a high electron density on the oxygen atom [22]; such a density that is higher with M = Na than with M = Mg. As a result, the mechanism for the MPVO reaction must be similar to that proposed for MgO. From the data of table 2 it follows that the efficiency with which hydrogen is transferred on NaMgP decreases as the temperature is raised from 673 to 773 K by effect of the ensuing hydrogenation that takes place irrespective of the MPV reaction. Similarly, the activity of $MgP_{(Cl,H)}$ can be ascribed to the presence of sodium–magnesium mixed phosphates, which were previously detected in related solids calcined at high temperatures [23].

Solid MgP_C, which consists of magnesium orthophosphate, $Mg_3(PO_4)_2$, is active in the dehydration of alcohols and also in the MPVO reaction. The fact that it is active in the hydrogen-transfer reaction suggests that magnesium orthophosphates possess the active sites required for the process; however, the sites that effect the dehydration of alcohols are more active than the previous ones, so, in some cases (e.g., with catalyst $MgP_{(Cl,H,C,w)}$), only the dehydration takes place. Like $MgPP_C$, $MgP_{(Cl,H,C,w)}$ possesses more acid sites (largely of the Brønsted type) than basic sites.

One of the major restrictions of the method used to titrate acidity and basicity is that sites are determined under conditions differing markedly from those of the reaction. However useful the information about the catalyst surface they provide may be, one can hardly relate in quantitative terms the acid and basic site values provided by the titrations to activity and selectivity in the catalysed reaction. This is specially difficult with solid catalysts since the reactions are influenced not only by the number and strength of catalyst sites, but also by their distances, arrangement and accessibility. Also, the mechanisms for many organic reactions on solid catalysts are poorly known and vary among catalysts. The MPVO reaction is bimolecular, so it may require various types of site to develop. This in turn will call for an appropriate distribution of sites and for appropriate distances among them if the transfer is to take place. Therefore, the number of active sites may be inadequate to establish a reliable correlation with catalytic activity. Some authors [11] have simplified the mechanistic problem by proposing the adsorption of the substrates (the alcohol and the ketone) on a single titanium atom in a β-titanium zeolite. The problem, however, may be complicated by the presence of a concerted bimolecular process. Even if the rate-determining step of the process (viz. the adsorption of the alcohol) were governed by acid sites, other types of acid sites present in the solid might help the reaction develop by favouring adsorption of the ketone and the transfer of a hydride ion. In such a case, the conversion results should exhibit a unity $X_{2\text{-HOL}}/X_{\text{CHONE}}$ ratio (i.e., the MPVO reaction would take place to the greatest possible extent, in the absence of side reactions). However, not all acid or basic surface sites can play a role in the MPVO process; some may lead to unimolecular reactions with more modest requirements. As a result of the formation of the corresponding byproducts, the $X_{2\text{-HOL}}/X_{\text{CHONE}}$ ratio would depart from unity and the hydrogen transfer would take place to a lesser extent. This has promoted the use of test reactions to determine catalyst acidity and basicity. The transformation of alcohols is a typical example. In this work, we carried out the transformation of 2-hexanol on the catalysts studied. The dehydration is believed to be catalysed by acid sites and the dehydrogenation by acid and basic sites – via a concerted mechanism [24], which, however, has been questioned [25]. Table 3 shows the results obtained in the transformation of 2-hexanol on the catalysts studied.

Table 3
Total conversion and selectivity towards hexanone (HONE) and hexenes (HENES) in the transformation of 2-hexanol on the catalysts studied.[a]

Catalyst	X_T (mol%)	S_{HONE}	S_{HENES}
MgP_C	97.1	0.02	0.98
$MgP_{(Cl,H)}$	12.7	0.73	0.21
$MgP_{(Cl,H,w)}$	61.5	0.20	0.79
NaMgP	13.0	0.99	0.01
$MgP_{(Cl,H,C,w)}$	100	0.01	0.99
$MgPP_C$	98.2	0.01	0.99
$MgP_{(OH,H)}$	100	0.03	0.96
MgO_C	41.3	0.69	0.15

[a] Reaction conditions: W/F (feed $\text{mol}^{-1}\,\text{h}\,\text{g}_{\text{cat}}$) = 5.65; N_2 flow rate 40 $\text{ml}\,\text{min}^{-1}$; amount of catalyst 0.175 g; feed rate 3.88 $\text{ml}\,\text{h}^{-1}$; $T = 773$ K, $t_{\text{reac}} = 120$ min.

A comparison of these results with those for the MPV reaction reveals a clear-cut correlation between activity in the latter and conversion to hexanone in the transformation of 2-hexanol, which confirms that activity in the MPV reaction is basicity dependent.

It should be noted that, unlike the other catalysts that are active in the MPVO reaction, solid MgP_C possesses no dehydrogenating ability; also, it is essentially acidic [4]. This exposes the differences between the dehydrogenation and the MPV reaction as 2-hexanone is only obtained if the acceptor (cyclohexanone) is present. Similarly, solid $MgP_{(Cl,H,w)}$ converts 2-hexanol preferentially into hexenes; in the presence of an acceptor such as cyclohexanone, however, the solid produces 2-hexanone virtually exclusively.

Just as the dehydrogenation of alcohols and the MPV reaction have been hypothesized to develop via mechanisms involving acid and basic sites, the dehydration of alcohols is believed to take place via a virtually concerted mechanism involving an acid site and a basic site at an appropriate distance on the catalyst surface. In this case, it is the C–O bond that is cleaved and the β hydrogen that anchors to the basic site. The acid and basic sites that take part in the dehydration need not be the same as those involved in the MPV reaction, however.

Under our operating conditions, the MPV reaction seems to take place in a concerted manner and at a lower temperature than the dehydrogenation of the alcohol acting as a donor; this suggests that adsorbed ketone in the vicinity of the alcohol favours its dehydrogenation and lowers the temperature at which the proton is released. Based on the mechanism of Kibby and Hall [26], the alcohol and the ketone are adsorbed on acid sites but require the presence of a basic site nearby. The transfer is bound to occur as depicted in figure 1.

The neighbouring basic site favours ionization of adsorbed alcohol and facilitates the hydride transfer to the ketone. In coordinating to a basic site, the proton weakens the O–H bond and facilitates the formation of the C=O

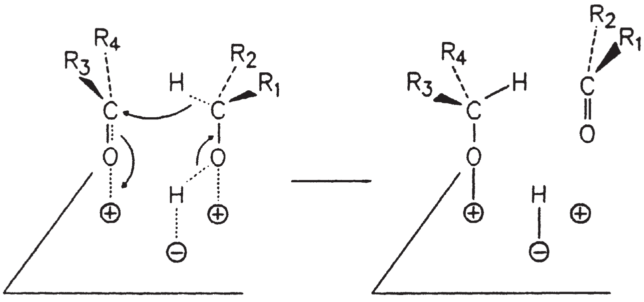


Figure 1. Schematic representation of the hydrogen transfer in the Meerwein–Ponndorf–Verley reaction.

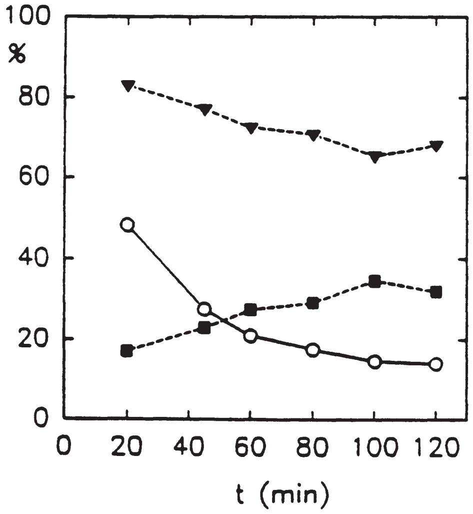


Figure 2. Overall conversion of 2-hexanol (donor) (○) and selectivity towards 2-hexanone (▼) and hexenes (■) as a function of time-on-stream for catalyst $\mathrm{MgP_C}$ at 673 K.

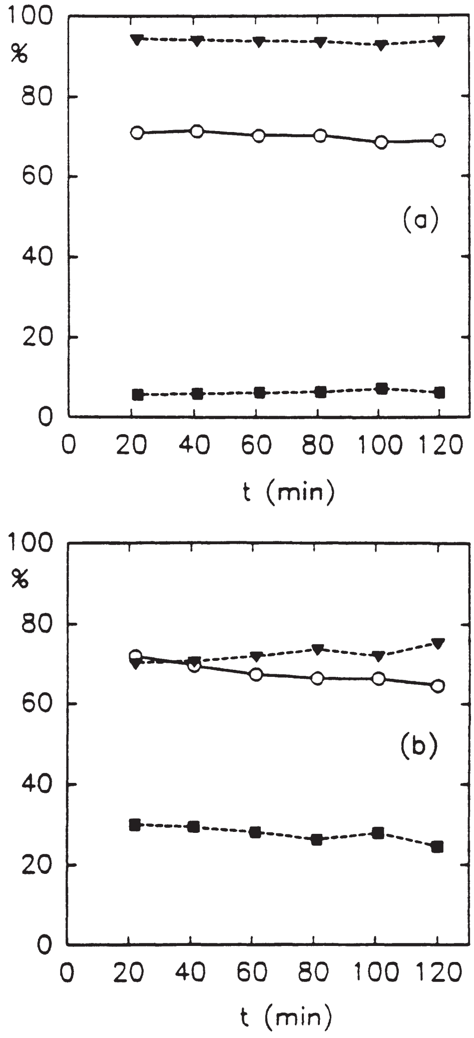


Figure 3. Overall conversion (○) and selectivity towards the alcohol or ketone (▼) and alkenes (■) for the donor (a) and acceptor (b) as a function of time-on-stream for catalyst $\mathrm{MgP_{(Cl,H,w)}}$ at 673 K.

bond and hence the hydride transfer. In the last step of the process, the proton adsorbed at the basic site attacks the alkoxide formed from the ketone.

When the catalyst contains a high proportion of acid sites, the alcohol is preferentially dehydrated; by contrast, the dehydrogenation and transfer reactions take place to a very small extent owing to the scarcity of basic sites to effect the hydride transfer. If the number of basic sites exceeds that of acid ones, then the dehydrogenation occurs as it requires only a fairly small number of acid sites.

Based on our results and on the proposed mechanism, the most suitable solids for the hydrogen transfer will be those with an acid-to-basic site ratio near 2. Although the phosphates $\mathrm{MgP_{(Cl,H)}}$, $\mathrm{MgP_{(Cl,H,w)}}$ and NaMgP meet this requirement, as noted earlier, the types of sites that are titrated by cyclohexylamine and phenol need not coincide with those that are catalytically active in this process.

Table 2 gives the activity and selectivity at a constant conversion obtained with the different catalysts studied. Figure 2 shows the conversion and selectivity profiles for catalyst $\mathrm{MgP_C}$ at 673 K. As can be seen, the catalyst is strongly deactivated by heating; its conversion falls from the beginning until it levels off at about 70% of the initial value. A similar effect is observed at 623 K and, in other solids (specifically, NaMgP and $\mathrm{MgP_{(Cl,H)}}$) over the range 623–673 K. At 773 K, however, the initial conversion remains constant throughout. With other catalysts, constant conversion is observed at lower temperatures (e.g., 723 K with $\mathrm{MgP_{(Cl,H)}}$ and 673 K with $\mathrm{MgP_{(Cl,H,w)}}$) (see figure 3).

The absence of coke residues and the fact that the extent of deactivation increases with decreasing temperature allow one to ascribe the deactivation to the gradual adsorption of some product on the catalyst as the reaction develops. TPD experiments performed during the dehydration–dehydrogenation of 2-propanol in previous work [27] revealed that, with basic catalysts such as MgO, acetone was retained on the catalyst surface after the reaction. The acetone was desorbed at a temperature between 473 and 773 K depending on the basic strength of the catalyst.

In fact, the likely origin of the deactivation in our case was the adsorption of ketones during the reaction. In order to confirm this assumption, we carried out the MPVO reaction on catalyst NaMgP at 673 K. The conversion dropped from about 45% at 20 min to 4.5% at 120 min. After stopping the feed stream to heat the catalyst at 773 K for 1 h, the temperature was reset to 673 K and the reaction resumed. The catalyst was found to regain its original conversion (about 42% after 20 min). A temperature above 673 K must therefore be used if deactivation of the catalysts in the MPVO reaction is to be avoided.

If the MPV reaction is taken to be a test for basicity [15,16], then, based on the catalytic activity data of table 2, solids MgO_C, $MgP_{(Cl,H)}$, NaMgP and $MgP_{(Cl,H,w)}$ behave as essentially basic catalysts, whereas solids MgP_C, $MgP_{(Cl,H,C,w)}$ and $MgP_{(OH,H)}$ behave as essentially acid catalysts.

4. Conclusion

Magnesium orthophosphates exhibit catalytic activity in the Meerwein–Ponndorf–Verley–Oppenauer reaction. Their activity and selectivity in the process depend on their structure and surface chemical properties. Some orthophosphates provide high selectivity and conversion, similar to those obtained with MgO. The reaction mechanism and active sites involved are also probably similar to those for MgO. Other magnesium orthophosphates are also active in the dehydration of alcohols, so they yield the corresponding alkenes as well. The most active among them dehydrate the donor alcohol almost completely, so virtually no hydrogen transfer can be observed. Magnesium pyrophosphate, $Mg_2P_2O_7$, is practically inactive in the MPVO reaction owing to its high acidity and very low basicity. The activity and selectivity of these catalysts in this reaction is related to their surface basicity.

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